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14. ABSTRACT

This program was directed to the use of highly electroactive, conjugated polymers as the active redox materials in electrochemical supercapacitors. Such materials include electrochemically polymerizable dimethyl substituted poly(3,4-propylenedioxythiophene) (PProDOT-Me2), poly(3,4-propylenedioxypyrrole) (PProDOP), poly(3,4-ethylenedioxythiophene) (PEDOT) for Type I or Type II supercapacitors, along with donor-acceptor-donor (D-A-D) polymers which provide reductive states for Type III supercapacitors. In addition, we have evaluated several solution-processable as alkoxy substituted PProDOTs and PProDOT-PEDOT co-polymers.

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Organization	Georgia Institute of Technology

Final Research Report

Technical Objectives

This program was directed to the use of highly electroactive, conjugated polymers as the active redox materials in electrochemical supercapacitors. Such materials include electrochemically polymerizable dimethyl substituted poly(3,4-propylenedioxythiophene) (PProDOT-Me$_2$), poly(3,4-propylenedioxypyrrole) (PProDOP), poly(3,4-ethylenedioxythiophene) (PEDOT) for Type I or Type II supercapacitors, along with donor-acceptor-donor (D-A-D) polymers which provide reductive states for Type III supercapacitors. In addition, we have evaluated several solution-processable as alkoxy substituted PProDOTs and PProDOT-PEDOT co-polymers. We have also explored methods to increase the substrate electrode surface area and determining the variables contributing to optimized materials and device performance.

Technical Approach

During this grant period our efforts have been focused on understanding the role of film morphology on the redox capacitance of dioxypyrroles and dioxythiophenes, optimizing and standardizing the electrochemical supercapacitor (ESC) devices that use these polymers as the active material, evaluating device electrolytes and current collector materials (both metal and carbon-based alternatives), designing D-A-D polymers for Type III devices, and finally evaluating the competitiveness of our electroactive polymer (EAP) based devices to verify that we can meet the necessary figures of merit. The structures for some of the evaluated polymers and monomers are shown in **Figure 1**.
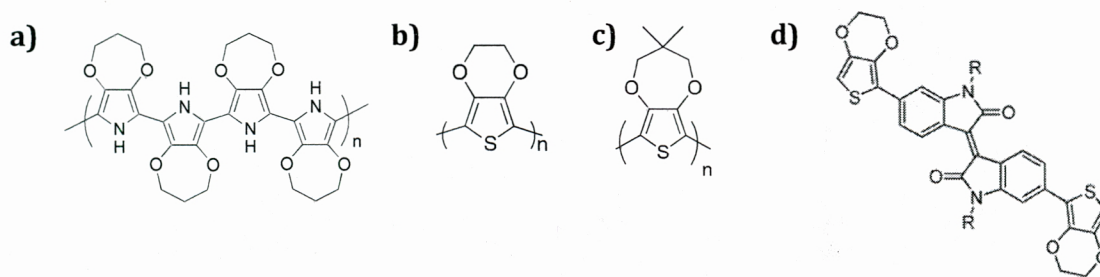
Figure 1. a) PProDOP, b) PEDOT, c) PProDOT-Me$_2$, d) BEDOT-isoindigo.

For electrochemically deposited EAPs, there are multiple variables that affect the redox capacitance and film morphology. In order to narrow down the number of experiments needed to determine the optimal deposition conditions for dioxythiophene-based polymers, we employed factorial *Design of Experiments* (DOE) approach using poly(3,4-propylenedioxythiophene) (PProDOT-Me$_2$) as our model compound. This allowed us to narrow down the most important deposition parameters that influence the film capacitance. This was done both for films deposited using potentiodynamic cycling (i.e. cyclic voltammetry) as well as for films deposited under constant potential conditions, as it will well known that these two polymerization conditions result in quite different film morphologies.

For our device optimization and standardization using PEDOT as the active material, we were then able to extend this concept and focus on the parameters that were expected to have the highest impact on film capacitance as estimated by the DOE methodology. By narrowing down the number of deposition parameters that were evaluated, we were instead able to focus our efforts on the device optimization and the evaluation of different device variables such as separator material, electrolyte, and type of current collector. Seeing that ESCs often used in applications that require non-caustic and non-flammable electrolytes we wanted to move away from organic electrolytes towards aqueous electrolytes and ionic liquids (IL). ILs are well-known for high electrochemical (> 4 V in some cases) and thermal stability (e.g. 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMI][BTI] can be sued between -35 and +60 °C), their low vapor pressure, and low flammability. As a result of their electrochemical stability ILs are noteworthy candidates for replacing organic gel electrolytes in Type I-IV EAP-based ESC devices.

In order to extend the voltage range of our ESCs we also evaluated D-A-D polymers as active materials in Type III and Type IV devices, as these types of polymers undergo both oxidative and reductive redox processes reversibly. In D-A-

D based ESCs, the charged state of the device is achieved when one EAP films is in the fully oxidized state and the other in a fully reduced state, in contrast to our devices that use all-donor polymers where one EAP is fully oxidized and the other is charge neutral (see **Figure 2**).
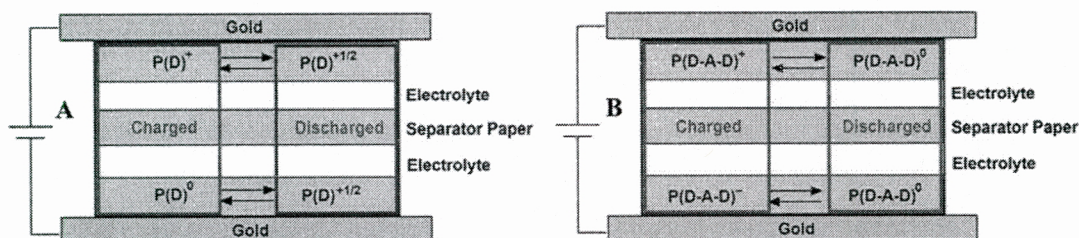

Figure 2. Device architecture for a) Type I/II EAP-based ESC and b) a Type III/IV EAP-based ESC.

In addition to developing flexible sandwich-type devices (device mass ca. 0.5 g), effort was also put into increasing the film and device capacitance by using highly conductive rough area electrodes to template high capacitance films by electropolymerization of the EAP onto these electrodes. This was explored by fabricating rough, planar gold electrodes through electrodeposition of gold from $KAuCl_4$ on thermally evaporated gold. While the surface area of the electrode was relatively high, this did not translate to higher polymer film surface areas or higher capacitance as the polymer film was very thick relative to the gold. Hence, we have evaluated reticulated vitreous carbon (RVC) as 3D electrodes material to not only increase the surface area, but also to be able to potentially increase the polymer loading. In addition to RVC that is a brittle electrode material, we have also evaluated different carbon nanotube (CNT) based current collectors, ranging from CNT mats, to CNT forests, to non-woven CNT fabric.

Progress Highlights from 2011-2013

Optimization and standardization of film deposition conditions and its effect on areal capacitance

There are a number of deposition variables that need to be tuned when electrochemically polymerizing EAPs, and there was not a unified understanding of how these different variables will affect the redox behavior and to what extent. As mentioned, just changing the polymerization method will result in films with quite

different morphologies on the microscale as we show in the SEM micrographs in **Figure 3a-b**. In addition to the polymerization method, the choice of solvent, electrolyte, film thickness, etc. are also expected to have a significant influence on the areal capacitance of an EAP film. We chose to evaluate seven deposition variables that are expected to affect the areal capacitance and by utilizing DOE we were able to reduce the number of experiments required to optimize the deposition conditions by an order of magnitude. We were also able to elucidate the mean effects of the chosen variables and quantify them as illustrated in the Pareto plots shown in **Figure 3c** where the magnitude of the bar indicates how large an effect a specific variable has on the output. For example, the areal capacitance of PProDOT-Me$_2$ films deposited under potentiostatic conditions (lower Pareto plot) was mainly affected by concentration of cycling electrolyte and far less so by the choice of electrolyte salt, for example.
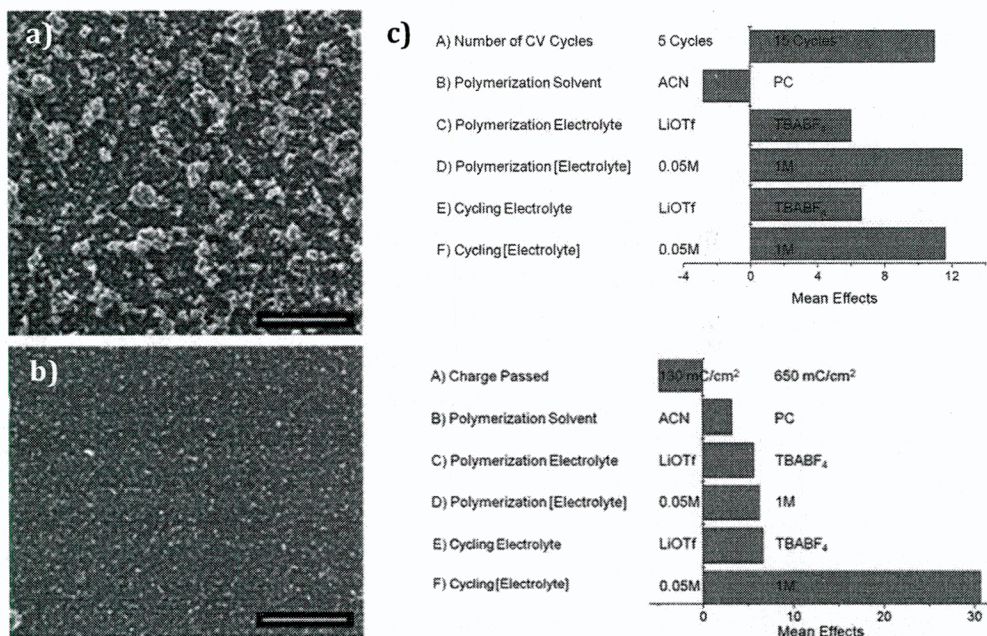

Figure 3. a) SEM micrograph of PProDOT-Me$_2$ electropolymerized by cyclic voltammetry b) SEM micrograph of PProDOT-Me$_2$ electropolymerized potentiostatically, and c) Pareto plots showing the effects of different deposition variables.

The optimized conditions allowed us to reproducibly be able to deposit films that were able to attain doping levels that were comparable, independent of

polymerization method, and among the highest observed for poly(3,4-alkylenedioxythiophenes).

More information and details can be found in the following publications:

Shen, D. E.; Estrada, L. A.; Osterholm, A. M.; Salazar, D. H.; Dyer, A. L.; Reynolds, J. R. *Understanding the effects of electrochemical parameters on the areal capacitance of electroactive polymers*, J. Mater. Chem. A, 2014, 7509.

Optimization of PEDOT devices

Based on our DOE studies on PProDOT-Me$_2$ the empirical optimization of PEDOT deposition was focused on (but not limited to) the type of electrolyte, electrolyte concentration, and electrochemical deposition method. We evaluated the areal capacitance of PEDOT deposited using both aqueous and organic electrolytes. PEDOT films deposited from organic or IL electrolytes consistently resulted in films with ~25 % higher areal capacitance values than similar films deposited from aqueous electrolytes. Seeing that the use of non-aqueous polymerization electrolytes not only resulted in higher film capacitances, but also in a broader available potential window, which is important for achieving high energy density, our PEDOT device optimization was focused on films deposited from organic or ionic liquid based electrolytes.

As mentioned, we wanted to focus on non-flammable device electrolytes, and as a result we did a thorough comparison of the [EMI][BTI] to a PMMA/LiBTI/PC gel electrolyte. Using the IL allowed us extend the voltage window for our Type I devices to 1.6 V without compromising the areal capacitance whereas devices using the gel electrolyte exhibited a decrease in device capacitance already at a voltage window of 1.2 V. This means that that the use of ILs as device electrolyte not only give us non-flammable devices but they are also able to outperform most Type I and Type II EAP-based ESCs that can be found in the literature. The possibility of extending the voltage window of a Type I ESC will result in an increased energy density, and ultimately considering laminated modules, the higher cell voltage will allow us to build modules using fewer layers.

In order to be able to assess if out optimized PEDOT/IL devices are competitive, their leakage current and self-discharge rate was compared to a commercially available Cellergy ESC that had a comparable capacitance as our PEDOT device. The

Cellergy ESC had a self-discharge rate of 8h and a leakage current of 5 µA whereas the corresponding values for our PEDOT ESC (assembled and evaluated in air) were 7h +/- 30 minutes and 2 µA, respectively. Another critical figure-of-merit is the cycling stability. Commercially available ESCs report cycling stabilities on the order of 10^6 charge/discharge cycles. In the EAP literature, a poor cycling stability is typically attributed to mechanical breakdown of EAP films as a result of the constant swelling/shrinking occurring as ions and solvent molecules are inserted/expelled during potential cycling. We monitored the cycling stability of a PEDOT/IL device over 400 000 cycles between 0 V and 1.0 V at 100 mV/s is shown in **Figure 4.** After an initial capacitance drop of 4.8 % during the first 10 000 cycles, we only observed a 3-4 % drop in capacitance for every 100 000 cycles. After 400 000 cycles, the device managed to retain 80 % of the initial capacitance.

To further demonstrate the efficacy of our devices, PEDOT ESCs were used as the sole power source to switch a polymer-based electrochromic device (ECD). ECDs were chosen for this demonstration for three reasons. First, ECDs have low operational power requirements and can be switched from a fully colored to a fully colorless state within a small voltage window. In the case of the ECD used here, full contrast was obtained in under 1.5 V. Second, EAP ECDs maintain their coloration without the need for a constant power supply, such as a battery. Finally, to realize electrochromic displays that are truly flexible, an equally flexible power source will be required for operation. Photographs (**Figure 4**) and spectra of the device in its fully colored and fully colorless states were found to be identical regardless if switched using a potentiostat or PEDOT ESCs.
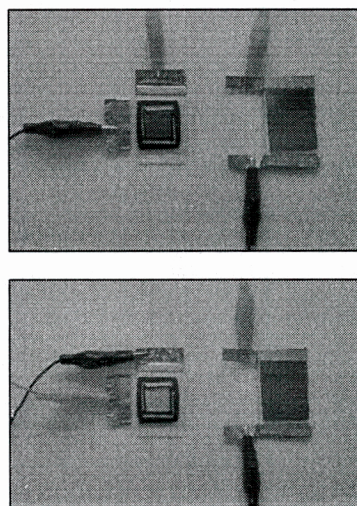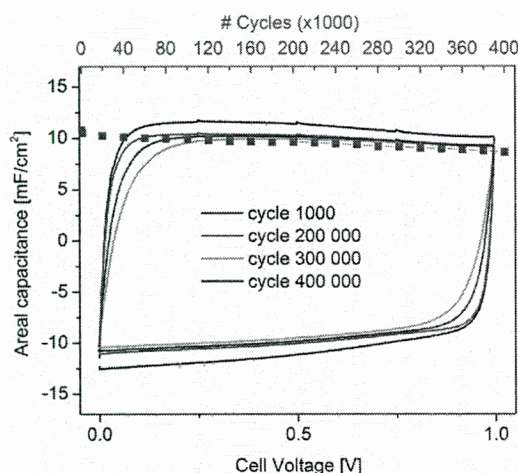

Figure 4. a) Stability test of a PEDOT/IL ESC and b) Photographs of a PEDOT/IL ESC switching an electrochromic device.

Osterholm A. M.; Shen, D. E.; Dyer, A. L.; Reynolds, J. R. *Optimization of PEDOT Films in Ionic Liquid Supercapacitors: Demonstration as a Power Source for Polymer Electrochromic Devices"*, ACS Appl. Mater. Interf., **2013**, 5, 13432.

Enhancing Aqueous Compatability

The optimization of environmentally benign, aqueous ESCs is still of high importance and we are currently designing and testing alternative aqueous-compatible polymers. Our approach for increasing the aqueous compatibility of our monomers and polymers is to introduce H-bonding between our EAPs and the water by funtionalizing PXDOTs with e.g. hydroxyl groups. Our first candidate was PProDOT–Me-MeOH (structure shown in **Figure 5**) that can be electropolymerized in organic electrolytes and then charged/discharged in organic as well as aqueous electrolytes without compromising the film capacitance, as shown in the CV in **Figure 5**. Current efforts are focusing on further increasing the aqueous compatibility of PXDOTs by increasing the number of hydroxyl groups on the side-chains.
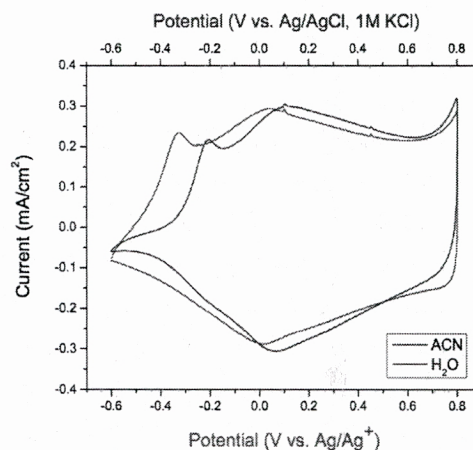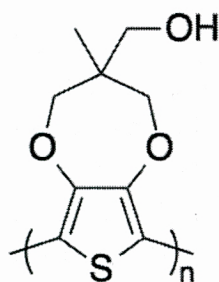

Figure 5. Structure of PProDOT-Me-MeOH and its cycling behavior in LiBTI/CAN (red trace) and in LiBTI/H_2O (blue trace).

More information and details can be found in the following publication:

D-A-D polymers for Type III and Type IV ESCs

D-A-D polymers have the advantage that they can be reversible oxidized and reduced electrochemically, which should make them ideal candidates for Type III/IV ESCs. Bisheteroarylenes provide an effective way to allow for these D-A-D polymers to be electrochemically polymerized. The donor moiety was chosen to be EDOT since we were familiar with its electropolymerization and the resulting polymers exhibit high conductivity and stability in their oxidized state. Isoindigo was evaluated as the acceptor moiety due to its straightforward synthesis, ambient stability, ease of derivatization, and deep frontier orbital energies. The structure of bis(3,4-ethylenedioxythien-2-yl)isoindigo (BEDOT-iI) is shown in **Figure 1d**. The electrochemically polymerized PBEDOT-iI can be reversible oxidized (p-doped) and reduced (n-doped) as shown in the CVs in **Figure 6a**. As can be seen, the oxidation process exhibits a capacitive CV (typical for all-donor dioxythiophene-based polymers) whereas the reduction process is highly Faradaic (common for D-A polymers). The clear advantage of the D-A-D approach is illustrated in the CV in **Figure 6b**, where Type III ESCs using PBEDOT-iI can use operating voltages as high as 2.5 V, however, because of the Faradaic nature of the reduction process the current in the device CV is not independent of voltage, as it is in our all-donor Type I devices.

The reason for the Faradaic reduction behavior was evaluated computationally using density functional theory (DFT) calculations carried out at the B3LYP/6-31G* level of theory. This data showed that the LUMO wave function is highly localized on the isoindigo unit whereas the HOMO wave function delocalizes across the conjugated backbone, see **Figure 6c**. The localization of the LUMO will result in charges being pinned and ultimately hampering n-type conductivity. From this study it became evident that the next generation of EAPs that are developed for Type III/IV ESCs should consist of units that generate a LUMO wave function that can delocalize along the polymer backbone, allowing for improved n-doping behavior as well as more capacitive charge/discharge profiles.
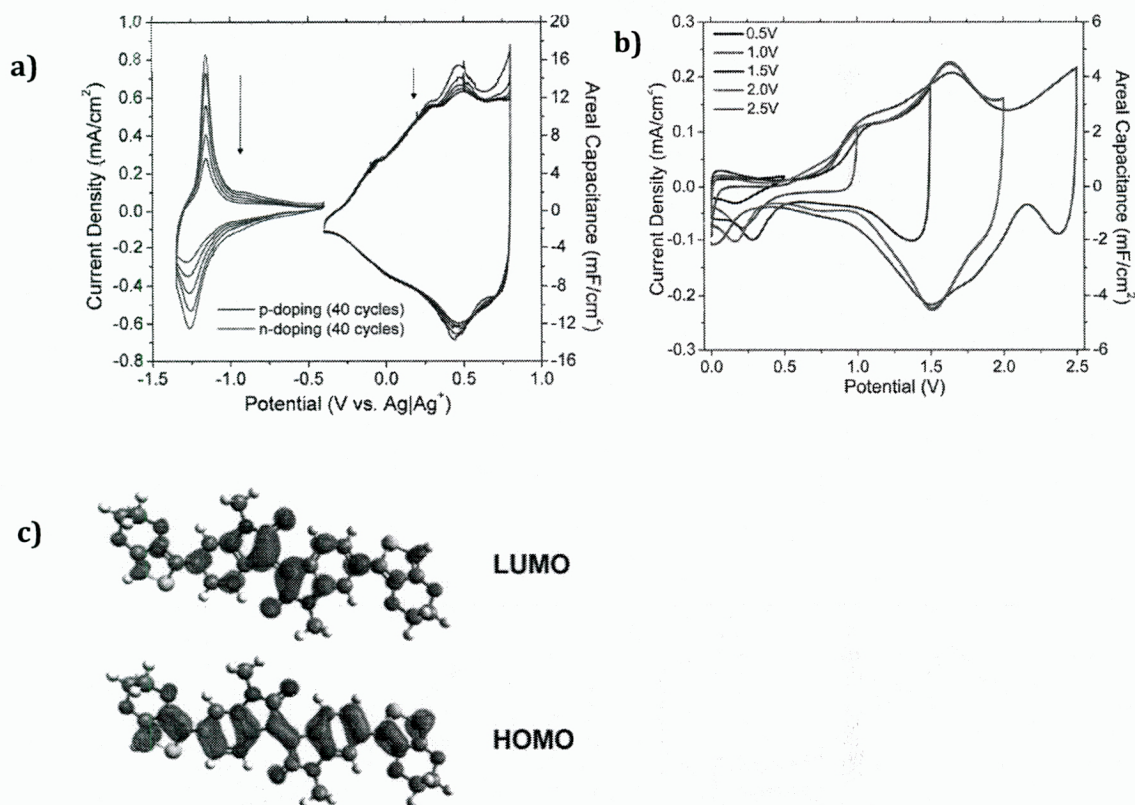
Figure 6. a) CV of a PBEDOT-iI film electrochemically polymerized on a Au electrode, b) Type III ESC operating from 0.5 to 2.5 V at 50 mV/s, and c) 6,6'-BEDOT-iI-Me2 frontier orbital maps.

More information and details can be found in the following publication:

Estrada, L. A.; Liu, D. Y.; Salazar, D. H.; Dyer, A. L.; Reynolds, J. R., *Poly[Bis-EDOT-Isoindigo]: An electroactive polymer applied to electrochemical supercapacitors*, Macromolecules, **2012**, **45**, 8211.

High surface area electrodes

One challenge for EAP based ESCs is to increase the amount of active material relative to the other components in the device (electrolyte, current collector, separator, etc.) since this would allow us to increase the specific mass capacitance of our ESCs. This has led us to evaluate different high surface area electrode materials, both metal based and carbon-based. This grant period saw finalization of work

using carbon nanotube based electrode materials carried out in the previous granting period in collaboration with Prof. Andrew Rinzler (University of Florida).

One of the initial approaches was to explore electrodeposition of Au on thermally evaporated Au. While the surface area of the electrode was relatively high and rough, this did not translate to higher polymer film surface areas or higher capacitance as the polymer film was very thick relative to the gold. For this reason we decided to evaluated reticulated vitreous carbon foam (RVC) as the other extreme of a high surface area material. RVC is an open-pore foam material with an exceptionally high void volume (90-97 %), high surface area ($\sim$50 cm^2/cm^3 for the tested foam), and low resistivity (32.3 x 10^{-2} ohm cm). The drawback with RVC is that it is a brittle material that cannot be incorporated into flexible ESCs, however, the large pores should allow us to increase the polymer loading compared to 2D current collectors. The electrode capacitance of the bare RVC foam (mass: 13 mg) was determined by CV to be 0.04 F/g. Coating the RVC foam with electrochemically deposited PEDOT increased the electrode mass capacitance to 8.7 F/g, *i.e.* a 217 time increase, this is shown in **Figure 7**. A challenge with porous electrodes is that there tends to be a large current and potential distribution throughout the electrode and this affected the charge/discharge rates and we were limited to discharge times on the order of 40-50 sec compared to 1-2 sec for PEDOT on planar Au.
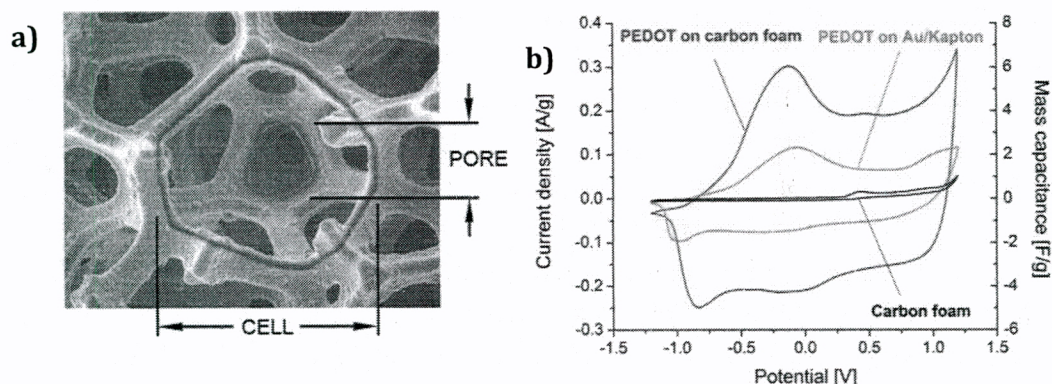

Figure 7. a) Micrograph of RVC foam and b) comparison of charge/discharge behavior of RVC foam electrode, PEDOT coated Au/Kapton electrode, and a PEDOT coated RVC foam electrode at 50 mV/s.

Because our goal is to develop devices that can discharge in less than 30 sec, we evaluated alternatives to RVC and we have tested several types on CNT electrodes. One approach was electropolymerizing ProDOP onto CNTs that had been treated with pyrene-funtionalized polyfluorene to improve the interfacial adhesion. The presence of the CNTs allowed for the electropolymerization of thicker PProDOP

films than using planar Au current collectors and ultimately resulting in a significant increase in the areal capacitance as shown in **Figure 8**. Using these electrodes we were able to decrease the discharge rate to around 5 sec, which is an improvement, compared to the RVC. Unfortunately, the ESCs prepared using the CNT electrodes showed a steady loss of capacitance to about 57% of the original value after 30 000+ charge/discharge cycles. However, the areal capacitance after 30k cycles was still 38% larger than the initial capacitance of the Au electrode devices, suggesting that the use of CNTs as current collectors is promising but alternative designs needed to be explored.
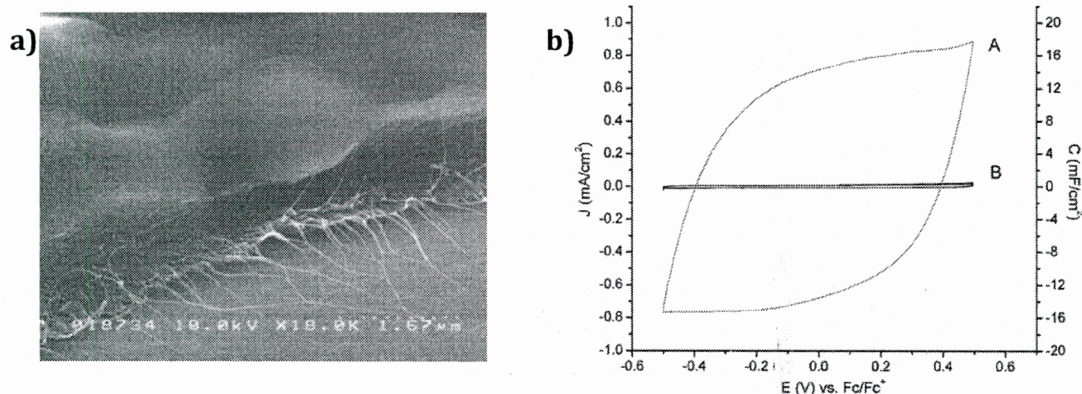

Figure 8. a) Micrograph of PProDOP film electropolymerized on a CNT mat and b) comparison of charge/discharge behavior of the bare CNT electrode (black trace) and a PProDOP coated CNT electrode.

During this grant period we feel that we have been able to show that dioxythiophene and dioxypyrrole polymers are competitive materials for ECS applications and we feel that the time has come to move away from electrochemical deposition towards more high-throughput coating methods such as spray coating or blade coating. A common problem with soluble homo-polymers is that they tend to have Faradaic CVs and narrower potential windows than electrochemically polymerized EAPs. Therefore, we set out to develop a new family of EDOT–ProDOT based co-polymers, as PEDOT is known for its capacitive redox behavior. **Figure 9** shows the structures and CVs of some of our new ProDOT-EDOT co-polymers compared to an alkoxy-funtionalized PProDOT homo-polymer where it is clearly seen that the incorporation of EDOT units gives us materials with highly capacitive redox behavior.
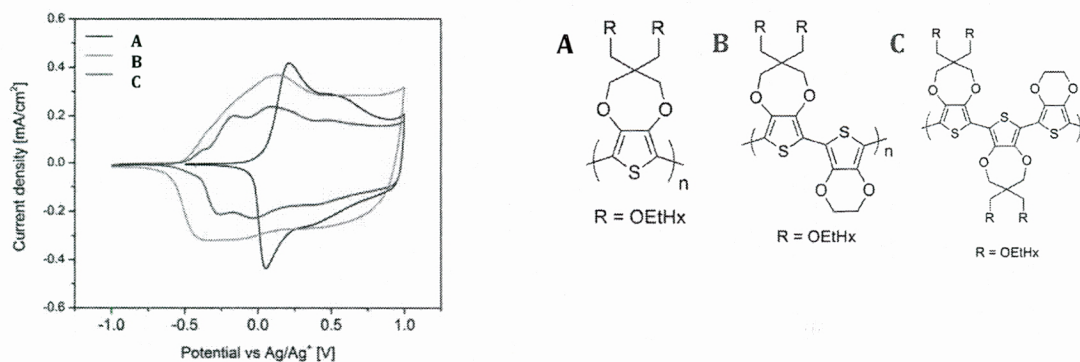
Figure 9. CVs of spray coated films of alkoxyfuntionalized PProDOT (structure A, black trace), poly(ProDOT-EDOT) (structure B, green trace), and poly(ProDOT$_2$-EDOT) (structure C, red trace).

We are currently working on incorporating these highly capacitive co-polymers into different, high surface area CNT materials, like CNT forest electrodes shown in **Figure 10**. These CNT forests can be spray coated with one of our new soluble polymers to improve the electrode capacitance. The CV in **Figure 10** compares a bare CNT forest electrode (black trace) to a CNT forest electrode that has been spray coated (red trace) with a ProDOT-EDOT co-polymer (structure B in **Figure 9**) where the improvement in electrode capacitance as a result of the polymer coating is clearly seen.
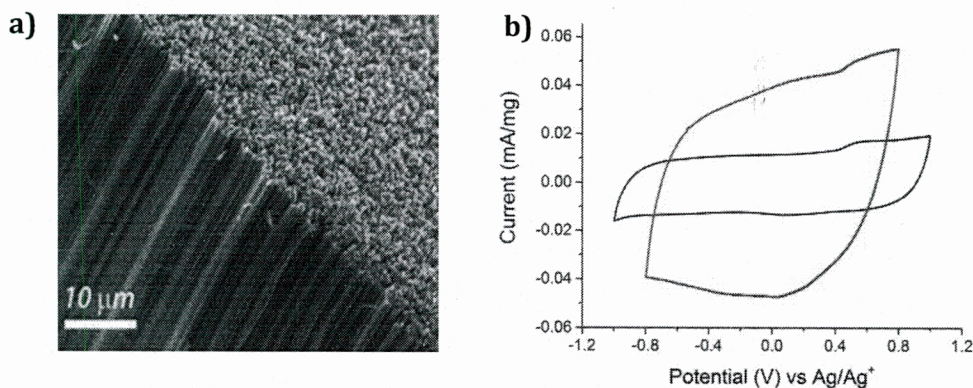

Figure 10. a) Micrograph of CNT forest electrodes and b) CV of bare CNT electrode (black trace) and CV of poly(ProDOT-EDOT) coated CNT forest electrode (red trace).